FORM 20 RW

Register of Wills of Allegheny County, Pennsylvania

Commonwealth of Pennsylvania, } SS: **No.** 165852
ALLEGHENY COUNTY

No. 020002396 of 2000

I, DAVID N. WECHT, ESQUIRE, Register of Wills in and for the County of Allegheny in the Commonwealth of Pennsylvania, DO HEREBY CERTIFY that on the 31ST day of MARCH , 2000 LETTERS LETTERS OF ADMINISTRATION on the Estate of THOMAS STEPHEN BRIMA

THOMAS S. BRIMA

, deceased, were granted to GWENDOLYN HAWK

having first been qualified well and truly to administer the same. And, I further certify that no revocation of said Letters appears of record in my office.

Date of Death FEBRUARY 22, 2000

Social Security No. 275-56-2351

Given under my hand and seal of office, at Pittsburgh

this 2ND day of MAY 2001

David N. Wecht

DAVID N. WECHT, ESQUIRE REGISTER OF WILLS

Paul K. [illegible]

CLERK

NOT VALID WITHOUT ORIGINAL SIGNATURE AND IMPRESSED SEAL

OIPE JC60 MAR 0 3 2004 PATENT & TRADEMARK OFFICE

Attorney's Docket No. 47003.000058 *Patent*

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: Brima et al.	:	
	:	Group No. : 1714
Serial No.: 10/043,934	:	
	:	Examiner: Katarzyna I. Wyrozebski Lee
Filed: January 11, 2002	:	

For: Manufacturing Inorganic Polymer Hybrids

DECLARATION OF DR. SEHYUN KIM UNDER 37 C.F.R. § 1.131

I, Sehyun Kim, am an inventor of the methods for Manufacturing Inorganic Polymer Hybrids that are disclosed and claimed in the above titled application. I received my BE in Materials Science and Engineering from Korea University, Seoul, Korea in 1982, and a Masters Degree and Ph.D. in Polymer Science from the University of Akron, Ohio in 1985 and 1990, respectively. Throughout graduate studies, I gained expertise in polymer science and engineering. I first became involved in an industrial scale polymer technology as Sr. Research Chemist at Fina Oil and Chemical Company (currently, AtoFina Petrochemical Company) in Deer Park, TX in 1990, and have been working in the technology field since then. I began working for Aristech Chemical Corporation (which became Sunoco Chemicals), in June 1998 in Product Development, and am currently employed at Sunoco Chemicals as Polypropylene Materials Scientist.

I and my co-inventors accomplished actual reduction to practice of the claimed methods of the present invention by September 1999, based on research accomplished in 1998 and1999 as shown by this Declaration and the attached Exhibits. Several of the attached Exhibits have been sanitized to remove references to proprietary information.

I began working on this project in 1998. Throughout the latter part of 1998 and through 1999, samples of hydrotalcite were prepared at the Aristech (Sunoco) Research and Technology Center in Pittsburgh, Pennsylvania. These samples were provided for experimental testing to determine if the materials performed to the required standards and to receive feedback for further research. Trials were completed in September of 1999. (See Exhibit A).

Attached as Exhibit B is a memorandum outlining the project involving the use of hydrotalcites as nanocomponents in polypropylene, and an associated research characterization report, indicating that TGA and DSC analyses of samples was completed on November 19, 1998. In particular, pages 15-17, tables 1-3 of the memorandum show the results of d-spacing and interlayer distance measurements on intercalated hydrotalcites and hydrotalcite/polymer blends. The results shown on Table 2 of the memorandum correspond to the analyses provided on the Research Characterization Report (Exhibit C), for several of the samples. This illustrates reduction to practice of the invention by as early as 1998/1999.

Based on the work contained in the above documents, we proceeded to prepare a patent application with the help of patent counsel in 2001. Work on various drafts of this application proceeded through the summer and fall of 2001. A final draft was approved and filed by counsel on January 11, 2002. Attached as Exhibit D are a series of e-mails in early November, 2001, indicating diligence in preparing the patent application.

I declare that the foregoing is true and correct, that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: February 27, 2004

Dr. Sehyun Kim

Fujii, Masaki

差出人: Migone, Ruben A.
送信日時: 1999年9月7日火曜日 午後 12:10
宛先: Fujii, Masaki
件名: RE: XRD of samples dried at different temperatures :sample #348-76A

Update on HT TGA-XRD experiments:
1. All TGA experiment are done.
2. All XRD spectrums except for the fresh sample are done. Analytical is experiencing a problem with the XRD's PC controlling machine. Once IT personnel find time to work on the problem and fix it, we will have this last spectrum done.
After this, I will write a small report on my findings.
Regards,
Rubén

-----Original Message-----
From: Fujii, Masaki
Sent: Monday, August 30, 1999 5:23 PM
To: Migone, Ruben A.
Cc: Gallaher, George R.
Subject: RE: XRD of samples dried at different temperatures :sample #348-76A

I definitely will need parallel XRD analysis of the interlayer spacing and change in the crystalline integrity when DSC/DTA analysis is conducted. I would like to ask you to conduct these analyses in close communication w/ George and Thomas.

What temperature range are you talking about when Al atoms are lost from the HT structure? PP is typically extruded at temperatures around the 200 through and 250 degrees C range. Is this the temperature range you are talking about? If so, will acidic intercalates such as p-aminobenzoic acid anion play a role of stabilizing the platy HT structure after exfoliation by explosive evaporation?

Masaki

-----Original Message-----
From: Migone, Ruben A.
Sent: Monday, August 30, 1999 3:22 PM
To: Fujii, Masaki
Cc: Gallaher, George R.
Subject: RE: XRD of samples dried at different temperatures :sample #348-76A

Thermal analysis as DSC/DTA will give you information, as TGA/EGA will, on temperature(s) at which the water/template is(are) released from the HT, but the information gathered by those techniques can not tell you about structural/composition changes. On the other side XRD analysis, can provide the interlayer spacing, and somehow will give and idea on sample loss of crystallinity (I mean when that is no obvious).
My personal experience with HT is that high temperatures may produce loss of Al from octahedrical to tetrahedrical positions, with the consequent loss of structure.
In order to keep the electrical neutrality of the solid when exposed to "explosive evaporation" under well-controlled extrusion conditions, you must have to provide an "anion medium" or the HT will fall apart.

Rubén

-----Original Message-----
From: Fujii, Masaki
Sent: Monday, August 30, 1999 3:46 PM
To: Migone, Ruben A.
Cc: Brima, Thomas S.; Gallaher, George R.; Kim, Sehyun; McLoughlin, Kimberly M.
Subject: RE: XRD of samples dried at different temperatures :sample #348-76A

I would like to know the behavior of the trapped water molecules up to the temperatures at which hydrotalcite is spray-dried and extruded with polymers in an extruder. My goal is to find temperatures at which the amount of trapped moisture is controlled to your desire. This way one might be able to use the trapped moisture for opening up the layered structure of hydrotalcite using the explosive evaporation of the water in the galleries under well-controlled extrusion conditions. For this purpose, thermal analysis such as DSC or DTA might be more informative.
Masaki

-----Original Message-----
From: Migone, Ruben A.
Sent: Friday, August 27, 1999 6:56 AM

To: Fujii, Masaki
Cc: Brima, Thomas S.; Gallaher, George R.
Subject: RE: XRD of samples dried at different temperatures :sample #348-76A

I think the samples should also be send to characterization by MAS-NMR. Looking for 27Al, could give indication of dealumination during heating (if any). Also 1H-NMR (if sampling manipulation can be done fast enough) would be of interest, for studying proton mobility within the layers.
Regards,
Rubén
PS: TGA study would take a week or so, while I can not give you a timeframe for XRD analysis.

-----Original Message-----
From: Fujii, Masaki
Sent: Thursday, August 26, 1999 3:55 PM
To: Brima, Thomas S.; Migone, Ruben A.
Cc: McLoughlin, Kimberly M.; Kim, Sehyun
Subject: RE: XRD of samples dried at different temperatures :sample #348-76A

I am looking forward to hearing from you interesting results soon.
Masaki

-----Original Message-----
From: Brima, Thomas S.
Sent: Thursday, August 26, 1999 9:55 AM
To: Migone, Ruben A.
Cc: Fujii, Masaki
Subject: XRD of samples dried at different temperatures :sample #348-76A

Ruben,
Please dry the above HT sample in the TGA instrument at the following temperatures under helium until constant weight is maintained over time: 90, 110, 130, 150, 170, 190C. Please use same ramp rate for each temperature. Samples dried at each temperature should have XRD done to determine d spacing.

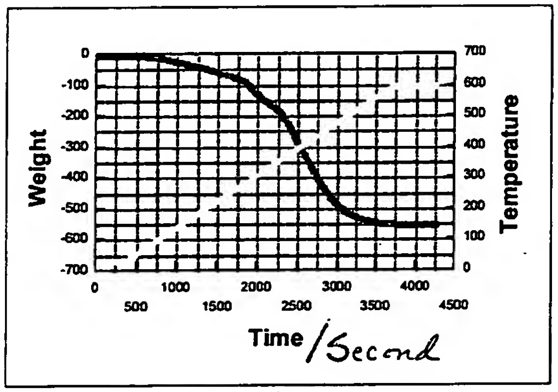
When I asked you if you could do this experiment for me you suggested we also look for (by Mass Spec.) compounds that are evolved during heat up. The following compounds would be possible: H_2O, NH_3, CO, CO_2, NO_2.

USE OF THERMAL GRAVIMETRIC ANALYSIS

TGA-EGA FOR HT ANALYSIS

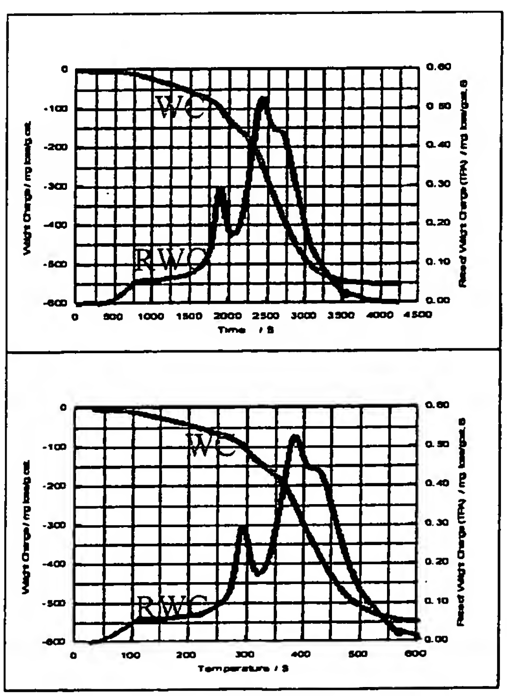
• TPD Method consist in heating the sample in a He stream, at constant heating rate while monitoring the change in weight.

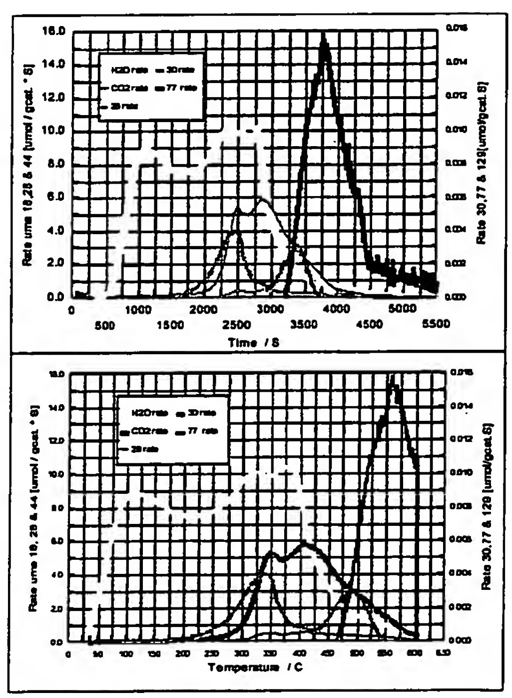
•To improve method sensitivity - EGA - a Mass Spectrometer was added.



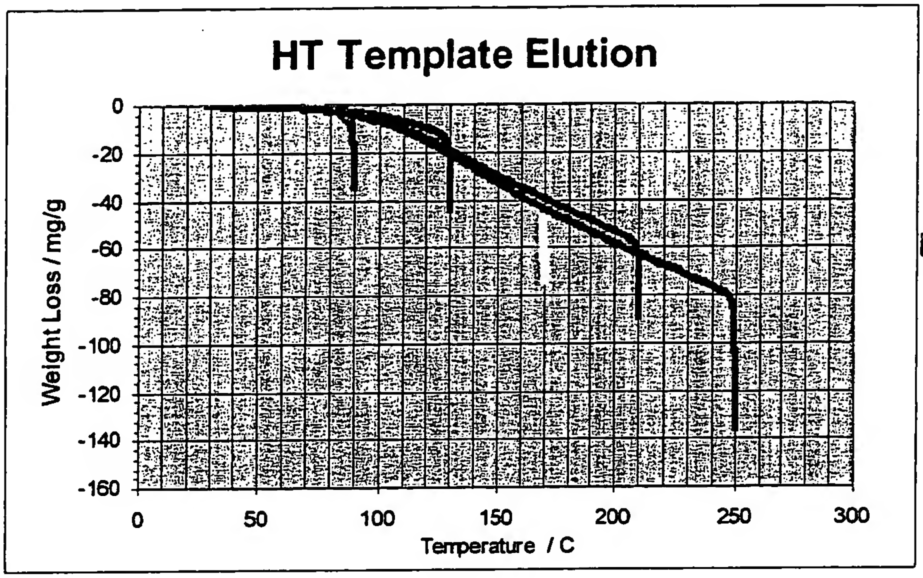
TGA data manipulation

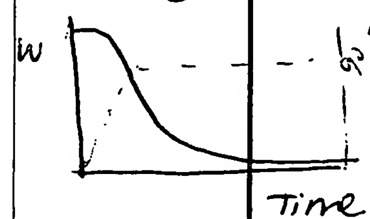
EGA (MS) data manipulation

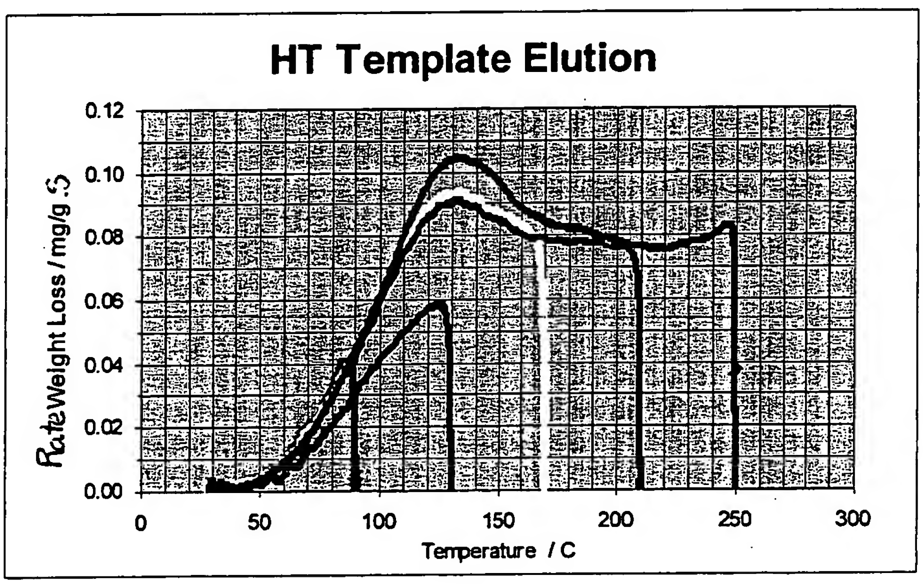




T Ramp:
35°C to T {90, 13[illegible], 17[illegible], 21[illegible], 2[illegible]}
1h @ T°C

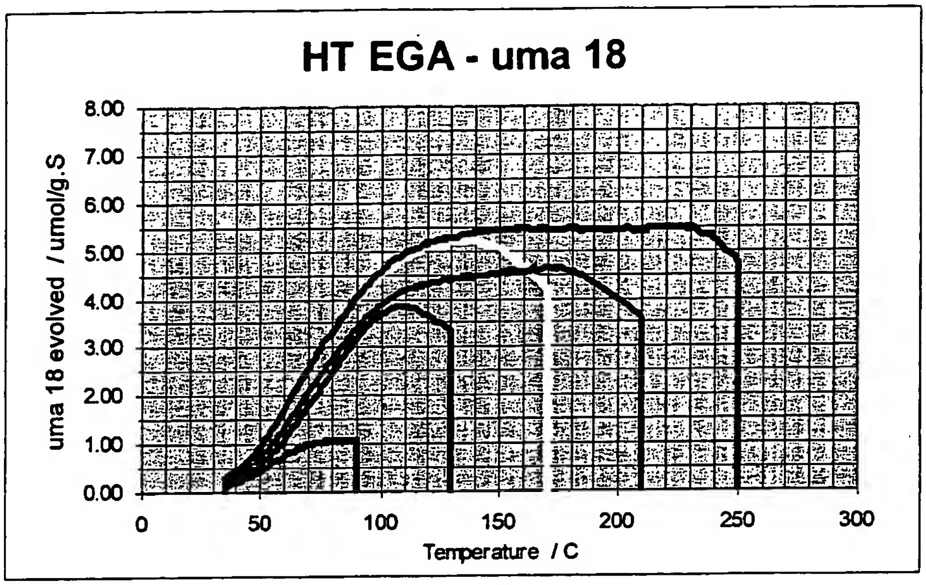


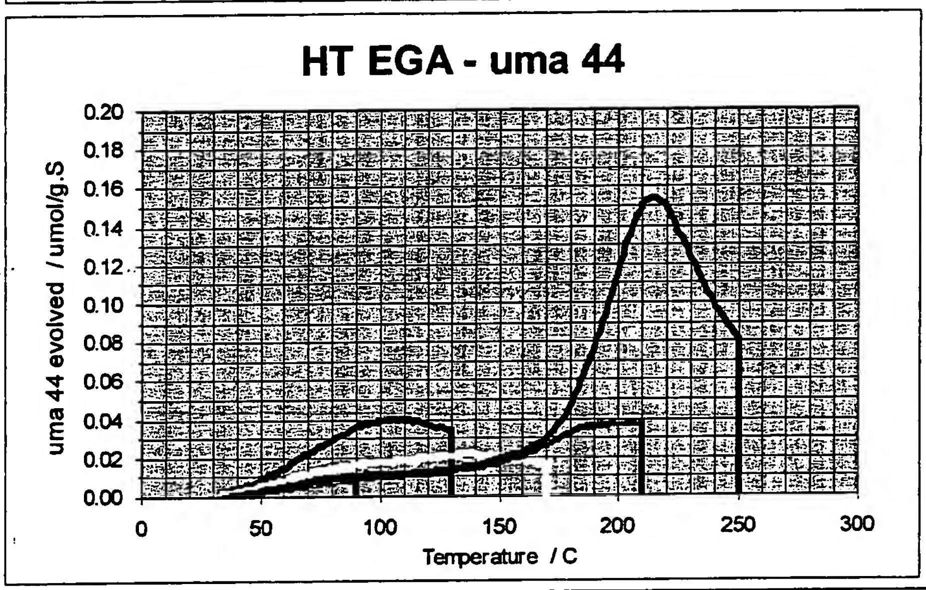


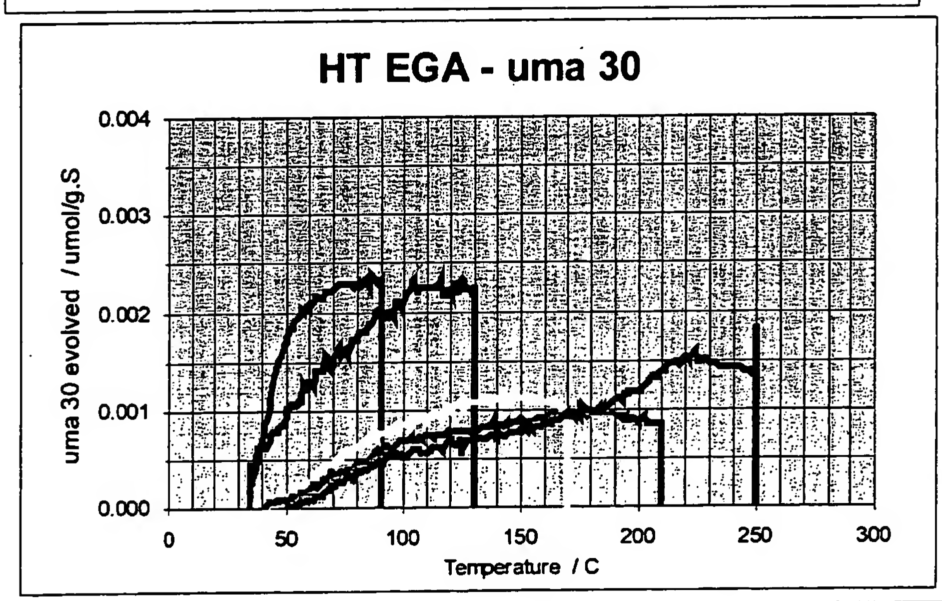


Temperature	W_l mg/gcat – initial	W_l^t mg/gcat	
90	34.2 ←	20.4 @ 90°C	= 13.8 (up till 90)
130	43.5	26.6	
170	74.1	29.1	
210	89.7	30.0	
250	135.3	52.2	
600	568	568	

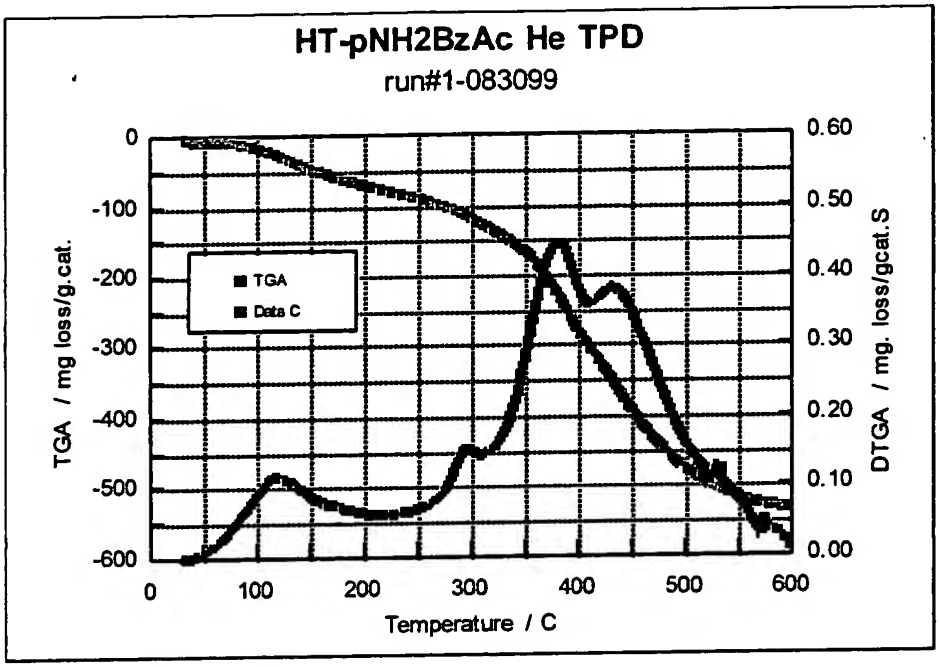
ram/090899a

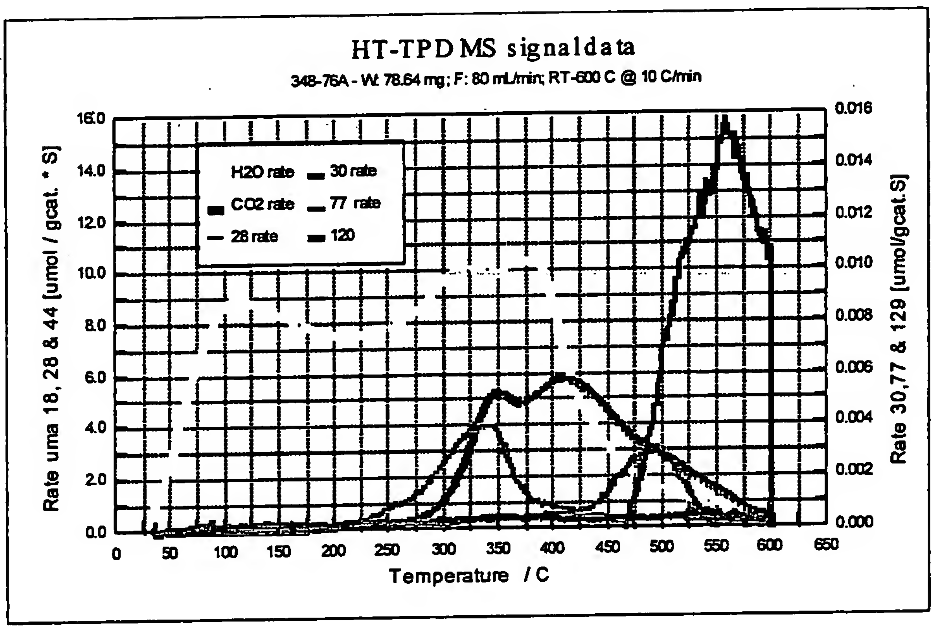

HT EGA - uma 18
uma 18 evolved / umol/g.S
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0
50
100
150
200
250
300
Temperature / C


HT EGA - uma 44
uma 44 evolved / umol/g.S
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
50
100
150
200
250
300
Temperature / C


HT EGA - uma 30
uma 30 evolved / umol/g.S
0.004
0.003
0.002
0.001
0.000
0
50
100
150
200
250
300
Temperature / C

ram/090899a





210-220 maximum operational temperature at atmospheric pressure

- XRD "***printed data***" showed no substantial differences between samples.

- "d-spacing" between the fist two basal planes matched the p-NH2BZAc molecule length calculated by K.Borden, this is 7.02 Å.

- "d-spacing" calculated as difference between the first basal plane and the brucite layer (4.31 Å) gives 11.1101 Å.

By: Thomas Brima
Nanocomposites

Date:
Project #: 0500-02

Subject: New hydrotalcites for Polymer applications

ABSTRACTS

A memo dated April 8, 1998 (1) outlined a project that involved the use of hydrotalcites (HTs) as nanocomposites in polypropylene. The Catalyst Group was to improve the Aristech Chemical Corporation process for the production of sheet-like hydrotalcites and to produce new hydrotalcites for incorporation into acrylic polymers and or polypropylene. The resulting enhancement of the polymer properties would then be evaluated. The goal was to prepare hydrotalcites with anions larger than C4, and also those with functional groups. Previous attempts to make such materials had been unsuccessful.

In this effort HTs with the following types of anions were successfully prepared and characterized by SEM and XRD:

1) Saturated carboxylates of C6,C8,C10 and C18 straight chain acids.
2) aromatics such as benzoate, chlorobenzoate, naphthoate, p-aminobenzoate and p-hydroxybenzoate.
3) Unsaturated carboxylates of acrylic, methacrylic and vinylacetic acids.

These compounds are novel in themselves

The preparations were made possible by using longer reaction time for contacting the aluminum source and the acids in water and/or the use of organic solvents, or in the acid melt.

Variation of experimental conditions.

Catapal alumina was found to be the preferred aluminum source for the preparation as it gave a more uniform HT (as indicated by SEM)

HTs obtained from the straight chain carboxylate homologs gave a good correlation between the chain length and the interlayer distance as measured by XRD.

Various batch type blends of high per cent hydrotalcites in polypropylene samples for compounding purposes were prepared from hydrotalcite (acetate anion) and polypropylene maleated polypropylene emulsion, and then

spray dried. Similar blends with HT of stearate, octanoate, acrylate and methacrylate in polypropylene were also prepared. These materials are available as sources for compounding and testing. Another master-batch was made by copolymerizing methyl methacrylate and an HT derived from methacrylic acid. The incorporation of these materials into polymers must still be performed before their value can be assessed.

INTRODUCTION

Hydrotalcites are generally considered derivatives of brucite, a layered magnesium hydroxide mineral that occurs naturally. They are made by substituting a trivalent metal cations, such as Al^{3+}, for some of the magnesium cations in the layer. The magnesium can also be substituted for with other divalent cations. This substitution results in a net positive charge in the layers(2), requiring an intercalating anion. The following general formula has been derived(3) for hydrotalcites: $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}\cdot{}_mH_2O]^{x-}$, where M^{2+} is the magnesium or other divalent cation, M^{3+} is the aluminum or other trivalent cation and A^{n-} is the anion. In addition to the anion, water is also contained in the lattice structure.

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A new group of hydrotalcites with a unique sheet-like morphology, invented(4) at Aristech Chemical Corporation, comprised of anions derived from C1 to C4 saturated carboxylic acids. Their general synthetic method involves the reaction of an aluminum source with a carboxylic acid in water followed by the reaction of the resulting mixture with a magnesium source. The approximate molar ratio of the reagents used is as follows: Mg:Al:anion equals 2:1:1, the anion being the carboxylate of the acid used. These hydrotalcites have a sheet-like distinguishing morphology as opposed to the hexagonal normally observed for the non-carboxylate anion hydrotalcites. The distance between the layers (as measured by d spacing) depends on the size of the anion. For example, the carboxylate hydrotalcites have the following d spacings (angstroms): formate 7.64, acetate 12.3, propionate 13.02 and isobutyrate 15.15(4).

US Pat No. 5,399,329

copy to background section

Traditional uses of hydrotalcites have included applications as catalysts or catalyst precursors, ion

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exchangers, absorbers, ion-scavengers, medical (as antacids). They have also been recent uses in polymer applications for various property enhancements, as shown in the following examples: Used in polypropylene with other additives to give good melt flow index, flexural modulus and Izod impact strength(5); used in ethylene-vinyl acetate copolymer to give a film with good adhesion and barrier properties(6); and used in linear low density polyethylene to result in a film with thermal insulation and tensile strength(7). In these applications, the naturally occurring hydrotalcites, which contain the carbonate anion, were used.

Our current goal has been to prepare and test suitable sheet-like hydrotalcites, as nanocomposites, in polymer applications. The anions of such hydrotalcites would make them compatible with or react with polymers. To date most nanocomposite polymer applications have to do with the use of pillared clays and the naturally occurring hydrotalcites. Compounded compositions of nylon-6 and 5% clay nanocomposites have been shown to exhibit a 40% higher tensile strength, 68% greater tensile modulus, 60% higher flexural strength and a 126% flexural modulus(8). Nanocomposites are believed to disperse in the polymer either in a disorderly fashion, intercalation; or by exfoliation, in which the nanolayers are regularly spaced in the polymer. Exfoliation is believed to lead to the improved polymer properties(9).

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This report covers the strategy for preparing new hydrotalcites with anions that a) are longer than four carbons, b) have reactive functional groups, c) have aromatic structures and, d) can result in large d spacings (> 12 angstroms). It also covers preparations of master-batch blends of polypropylene and hydrotalcites that would be easily processed with other polymers of interest.

MATERIAL AND EXPEIMENTAL WORK

Aluminum source: 1) Catapal ® alumina which is aluminum oxide monohydroxide obtained from Vista Chemical Corporation.

2) Flash Calcined Alumina (FCA) from LaRoche Industries.

Magnesium source: Martin Marietta Magnesia Specialties Inc. Magchem 200D (a high purity, highly reactive magnesium oxide powder.

Acids used were obtained from Aldrich Chemical Company.

Maleated nonionic polypropylene emulsion from Chemcor containing 39-41% non-volatiles, Trade Name: 'Poly Emulsion 43N40' was used in the HT-polypropylene blend preparation.

The scanning electron microscopy (SEM) analyses of the HT samples was carried out by RJ Lee Group, Inc. The requested analyses required collecting photomicrographs in both secondary electron imaging (SEI) and transmission electron imaging (TEI) of typical particles in the samples. Three different typical particles of each sample were micrographed at magnifications ranging from 5,000X to 50,000X depending on the size of the particles.

method of making

HT PREPARATION

The preparation was carried out in two steps, the reaction of the anion source with the alumina source followed by the reaction of this mixture with magnesium oxide. The first leg of the preparation was carried out in water, organic solvent or in the melt. The second step was always carried out in water. Experimental preparations were carried out first and, when successful, large scale preparations generally followed.

Claim these

1) Water medium

Trial preparations were carried out as follows:
Catapal alumina (.26 moles) was suspended in 500 ml deionized water in a 4-liter beaker and acid (.23 moles) was added to the stirred suspension. The beaker was fitted with a crystallizing dish filled with ice water to condense volatiles in the beaker as it was heated to 75-85C and maintained for 4 to 8 hours. At the end of the period the magnesium oxide (.44 moles) was then added, followed by 1.5 liters of deionized water. The mixture was then heated to 90-95C and maintained for 4 to 8 hours. It was then let cool down to room temperature overnight under stirring. The resulting material was dried in one of two ways: a) in an air oven at 130C until semi-dry solid obtained which was

further dried in a vacuum oven at 80C overnight, b) spray dry at approximately 200C inlet temperature and about 100C outlet. The final powder was the intended hydrotalcite.

2) Preparations using organic solvents
The reaction of the alumina and acids that are not water soluble or miscible (e.g. stearic acid) were sometimes carried out in organic solvents such as refluxing hexane. For example, Catapal alumina (.26 moles) was suspended in 200 mls hexane in a 4-liter beaker and acid (.23 moles) was added to the stirred suspension. The beaker was fitted with a crystallizing dish filled with ice water to condense volatiles in the beaker as it was heated to about 65C and maintained for 4 to 8 hours. The solvent was removed by evaporation or filtration, then water was added to the resulting residue. Under vigorous stirring, magnesium oxide (0.44 moles) was added in portions then the mixture was heated to about 90-95C and maintained there for 4 to 8 hours. The product isolation was then carried as in step 1 above.

no suggestion to use organic solvents

3) In acid melt
A beaker containing required amount of solid acid (e.g. stearic acid) was heated on an oil bath until the acid melts. The desired stoichiometric amount alumina was then added in small portions to the well-stirred melt. The condition was maintained for about two or more hours. Water is then added to the product, stirred to an even consistency then magnesium oxide was added and the rest of the reaction finished as in step 1 above.

Large Scale Preparations
Large-scale preparations were carried out in a 4-liter stainless steel beaker with the mixture stirred mechanically and heated on a hotplate. The amounts used in these preparations were four to six-fold increase of the amounts in the experimental preparations.

Material Characterizations
All the HT powder prepared were analyzed by XRD for the X-ray peak positions, intensities and d spacings. The d spacings of 10 or higher were used as criteria for further analysis by SEM. Samples for SEM analysis were sent to RJ Lee Group, Inc. (Monroeville, PA). Each sample was briefly scanned to evaluate particle loading and to identify particle types. Three typical particles were selected for photomicrographs using both SEI (secondary electron imaging)

and TEI (transmission electron imaging). Magnifications were selected based on the size of particles observed and ranged from 5,000X to 50,000X. The photomicrographs were used to determine whether the morphology was cabbage-like (also known as sheet-like) or not. They were also used to determine the dimensions of the particles.

Preparation of blends

The blends of HT and polypropylene were prepared as follows:

Required amount of the HT was added to water that would result in about 3% (weight, maximum for gel formation) in water. The temperature of the mixture was raised to about 40 to 60C and the required amount of the polypropylene emulsion (depending desired blend composition) was slowly added to the gel under high stirring. Enough water is then added to keep the mixture fluid. It was then heated to about 80C and maintained for one hour then let cool down to room temperature under continued stirring overnight. The mixture was then spray dried at an inlet temperature of 230C and an out of 90-105C. Each of the blends was then sent for XRD, DSC and TGA analyses.

Blends of stearic acid, octanoic acid, methyl methacrylic acid and acrylic acid HTs were also made in the manner above. Some were also prepared in a manner that required the addition of the polypropylene emulsion to the unisolated HT in the preparations outlined in preparation Step 3 above. The resulting was then isolated by spray drying in usual manner.

Methyl methacrylate (MMA) polymerization in presence of HT

The reactions were carried in a 1-liter Chemco reactor under 20 psig nitrogen at a stirring rate of 400 rpm. The amounts of MMA, HT and reaction temperatures are as shown in Table 4. In each case the reactor was charged with 460 cc water, 100g MMA and desired amount of HT and is purged with nitrogen then pressurized. Initiator, AIBN (2,2-azobisisobutyronitrile) (0.5g), surfactant (Aerosol OT 75%, 2.5g) were dissolved in 470 g MMA and the solution was pumped (88cc/hr) into the reactor which had been heated to 70C. Each reaction continued until the stirring became difficult due to solid product clumps. At this point the MMA feeding was stopped and temperature was maintained for about 30 minutes to react residual MMA. After the reactor

cooled to room temperature polymer chunks were taken out and let dry at room temperature in the hood. The amounts of polymer obtained are as shown in the Table 4.

is this a brand name?

Spray drying method

The Niro 2-fluid nozzle spray dryer was used with the following settings: heat at 5.5, air pressure to the nozzle was 1 bar and the inlet temperature was maintained at desired set range 200-230C by varying the liquid feed rate (4-5 liters/ hr). Water was fed to the dryer after temperature stabilized to estimate the required feed rate and also to remove material possibly left behind from previous use.

RESULTS AND DISCUSSION

In previous Aristech research, sheet-like HTs were prepared in aqueous medium first by reacting Catapal alumina with a carboxylic acid at about 60C for a half hour followed by the addition of the magnesium oxide and temperature raised to 95C for about 6 hours. On drying the resulting gel HT is then obtained. This method worked well for most of the water-soluble carboxylic acids such as C1 to C4 carboxylic acids (not for those acids that are water insoluble). In fact with butyric acid (C4 acid) only limited success resulted.

In the current work, it was realized that the success in preparing each HT depended greatly on the complete reaction of the aluminum source with the specific carboxylic acid (Step 1 in preparation outline). With this knowledge, changes were made for preparing HTs from longer chain (>C4) carboxylic acids and water insoluble aromatic acids. Three approaches were taken to improve step 1: 1) the reaction time for alumina and the acid was increased from 30 minutes to 4 to 8 hours, 2) use of inert organic solvents for reacting water insoluble organic carboxylic acids with alumina, and 3) carrying out this reaction in the melt of the carboxylic acid. These steps were found crucial in the success of the preparation and the homogeneity of the final product.

Steps in HT preparation:

Step 1: Catapal alumina (AlO(OH) or FCA + Carboxylic Acid → Intermediate

60-75C, 4-8 hours

Step 2: Intermediate (in water) + Magnesia → HT gel

90-95C, 4-8 hours

Step 3: Dry (evaporate /dry under vacuum, filter/dry under vacuum or spray dry)

For example, stearic acid HT was prepared by all three methods. In water medium, smaller than usual amounts of water was used, otherwise the acid floated above the alumina suspension in the water thus slowing down the reaction rate. The product of the reaction is a greasy oil that is denser than the medium, and thus settles to the bottom of the reaction vessel. In such a medium some of the alumina and the free acid may get trapped and either not react or react only very slowly because mixing of these reagents now becomes highly limited. The HT by this method was not very homogeneous (Appendix A).

When this reaction was carried out in hexane, faster and exothermic reaction occurred, resulting in an intermediate soluble in the medium. A disadvantage of this step, however, is the need to remove the solvent before the reaction of the product with magnesia (Step 2 in preparation outline); this step has to be carried out in water. By this method a homogeneous HT with seemingly smaller particle size (as indicated by SEM, see Appendix B) and larger d spacing value was obtained.

A couple attempts were made to carry out the first reaction in the melt. The problem with this method is similar to the water medium in that the product is also greasy. The reaction rate was, however, much faster. Under better mixing than used here one can be expect a more complete reaction than in the water medium. This could be an economical method of preparing HTs of solid fatty acids that have moderate melting temperatures. It can also be faster than either the water medium due to the faster reaction rate or the organic solvent medium because of the need to remove the organic.

With longer reaction times for Step 1, HTs of the following anion sources were successfully prepared (Appendix C) in water medium: Methacrylic, acrylic, vinylacetic, benzoic, ethanesulfonic, lactic and p-aminobenzoic acids. Other preparations carried out in the water medium, which did not result in HTs with desired morphology (Appendix D), were from the following anion sources: glycolic acid, lactic acid and gamma-Butyrolactone. One explanation for the failure to produce desired HTs with these water soluble anion sources is the possibility of cross-linking between the layers due to the existence of double anions (carboxylate and hydroxylic) as indicated by solid state NMR.

HT ANALYSES BY XRD AND SEM

Each HT prepared was analyzed by XRD and other analyses carried out depended on the d spacing obtained from the XRD. The d-spacing is an indication of the distance between the layers in the HT, which in turn, can depend on the size and shape of the anion in the material. The concept that HTs with larger d spacing would mix with or exfoliate in polymers, led us to seek those with larger anions or anions with long carbon chains. Graph 1 shows that as the number of carbons in the anion increased so did the HT interlayer distance, which equals the d spacing minus the brucite thickness (4.7angstroms). In fact there is a good correlation between the number of carbons (at least up to C10) in the anion and the interlayer distance. There seems to be little or no difference if the anion is unsaturated or not in terms of the effect of carbon number and the interlayer distance. The highest interlayer distance obtained for stearic acid (Table 1) is 21.6 angstroms, which does not fit well on the graph. A predicted fit is 26.0, suggesting perhaps that beyond certain length of carbons there is enough flexibility in the carbon backbone to cause this deviation.

Except in rare cases, only materials, which had d spacing equal to, or higher than, 12 angstroms (d spacing for acetic acid HT), were sent to RJ Lee Group, Inc. for SEM analysis. The requested analyses required collecting photomicrographs in both secondary electron imaging (SEI) and transmission electron imaging (TEI) of typical particles in the samples. Three different typical particles of each sample were micrographed at magnifications ranging

from 5,000X to 50,000X depending on the size of the particles. From the SEM, the morphology and the particle size of the HT were obtained.

In accord with a previous patent(1), the cabbage (also referred as sheet-like) morphology was desired. Excellent such morphology was obtained for the new HTs prepared from the following acids: acrylic, methacrylic, vinylacetic, benzoic, octanoic, ethanesulfonic and chlorobenzoic acids (Appendix E). Other new HTs that had morphology described as semi-cabbage were those derived from the following anion sources: decanoic acid, stearic acid, mixed stearic, acrylic and acetic acids; mixed acetic, hexanoic and stearic acids; and naphthoic acid. By semi-cabbage one or two of the three typical particles selected, has the cabbage morphology. Possible reason for this morphology is that the size or shape the anions cannot conform to the true cabbage formation within the crystal structure. Also the long anion carbon chains and the interlayer water molecule in the HT structures may repel each other leading to distortion in the crystal structure. It is also possible that incomplete reaction of the alumina in Step 1 of the preparation outline can also lead to the semi-cabbage morphology.

??

In accord with the corroboration with) in the development and production of any new HTs, a few preparations were made with methacrylic and acrylic acids and flash calcined alumina (FCA). The SEM of the final products and made HT (acetate anion), HTC-0498-10, all gave a morphology can at best be described as semi-cabbage. The SEM may indicate that more than one aluminum compound exists in FCA or that its reactivity with the acid is lower compared to Catapal alumina. The d spacing for HTC-0498-10 was also 9.7 compared to 12.0 for a similar HT prepared at Aristech laboratory from Catapal alumina and acetic acid.

The average sizes (microns) of the particles were measured using the scales given in SEM micrographs. Because of intended use of the HTs the smaller particle size is preferred. The particles were generally (Table 1) in the nanometer ranges. The methods of drying the HT did not seem to affect the particle size.

Solid CP-MAS C^{13} NMR analyses of some of the HTs (Appendix F) indicate that the acids used in the preparations were indeed carboxylate, in the majority of cases. In a few instances however, both the free acid and the corresponding anion were present, indicating incomplete reaction in the first step.

Preparation of HT-polypropylene blends

Two approaches were taken to prepare blends of HT with the Chemcor polypropylene emulsion: 1) regelling finished HT in water, mixing with the emulsion, and then spray dry, 2) adding the emulsion to the prepared HT before spray drying to obtain the blend. Both of these approaches were tested to ensure feasibility. Blends with HTC-0498-10 from 5 to 81% (by weight) in the solid weight of polypropylene were prepared (Table 2) and analyzed by XRD, DSC and SEM. HTC-0498 had a limited regelling concentration of about 3% in warm water. This amount is much lower than the 8-10% claimed by in their virgin gel before spray drying. This low concentration would require the use of large reactors if this method of blend preparation were used. This method was also used for some of the HTs we had previously prepared (Table 3), namely those from octanoic acid, vinylacetic acid, stearic acid and mixed acids (acetic, hexanoic and stearic). These materials did not have the regelling problem associated with HTC-0498-10, which became very difficult to stir when the HT concentration was much above 3%. The approach of adding the polypropylene emulsion as a final step in the preparation of HT before spray drying was tested with HTs prepared from acrylic and methacrylic acids (Table 3).

The XRD analysis of the blends made from HTC-0498-10 indicated a substantial decrease in d spacing from about 9.7 to 6.3 angstroms as the polypropylene got higher than 60% (Table 2), but increased when the level was about 19%. The reason for this drop may be due to possible exfoliation or dispersion of the HT in the polymer matrix. With the longer carbon chain HTs, the effect of the blend composition on the d spacings was mixed. With blends of HTs of acrylic, methacrylic, vinylacetic and stearic acids there were drops (Table 3) in the d spacings of 17.5, 17.4, 11.4, and 35.2 % respectively even at HT compositions ranging from 38-59%. For octanoic acid and mixed acids (acetic, hexanoic and stearic acids) the d spacings for the blends increased respectively by 16.3 and 3.7% based on the HTs from which they were derived. These results may suggest

a lack of uniform blending of the HTs with the polypropylene or, that the size of the anion has a different influence on the d spacing in the blend. On the other hand blends made from unisolated HTs (acrylic and methacrylic acids) and the polypropylene emulsion had similar drops in the d spacings.

The SEM micrographs of the blends (Table 3) of HTs of octanoic, stearic and mixed acids and polypropylene all had what might be termed doughnut morphology (Appendix G). The SEM micrograph for the methacrylic acid analog however did not have the doughnut morphology (Appendix H) and was not what can be referred to as semi-cabbage. The dough-nut formation may be explained as arising from the hydrophilic portion of the HT forming a circular core while the hydrophobic portion, which comprise of stearate or octanoate anion mixed with the polymer matrix, surround the circular core. The sizes of the doughnut particles range in radius from 2-3 microns and, the size of the methacrylic acid derived HT-polypropylene blend averaged 5X3 angstroms. SEM of sample #360-72, a blend containing about 81% HT (Table 2), showed a cabbage morphology that was even better than that of the HT from which it was obtained. The SEM of similar blend with 5% HT (sample #360-74) however, had a doughnut morphology (Appendix I). The latter blend may have had the HT so highly dispersed in the polymer matrix that it probably no longer existed in a layered form.

TGA analysis of blends made from HTC-0498-10 and polypropylene gave %residue that would be indicative of the amount of HT in the material. The values (Table 2) increased with the %HT in the preparation, and for the most part represent nonvolatile materials that remain after heating the sample to elevated temperatures (Appendix J).

The DSC transition temperatures in the table represent temperature at which phase changes take place in the blend and are indicative of minimum required temperature for processing these materials in polymer applications. The first phase transition temperature occurs at approximately 150C for the blends. Some of these materials had lower transition temperatures that were due to loss of water.

Similarly, the %residue from TGA for HTs with anions other than acetate (Table 3) were also in line with the %HT in the blends when corrections are made for the contribution

for the weight of the anion. The DSC transition temperatures for the materials were also similar to those derived from HTC-0498-10, and first transition temperatures ranged from 148-152C. These materials can therefore be processed with polyolefins at normal temperatures.

HT-MMA copolymerization

The aim of copolymerizing the HT of methacrylic acid with methyl methacrylate was to prepare master-batch materials from which blends with polyolefins such as polypropylene can be prepared and tested. With the surfactant Aerosol OT (75%), the copolymer was expected to be evenly slurried in the water medium in which the reaction was carried out. In all the experiments slurry formation occurred only at the beginning of the polymerization. As the polymer amount increased, the suspended particles coalesced into a ball or chunks that would eventually force the early termination of the polymerization because of difficulty with stirring. In all three attempts the product was a tan, tough and stiff polymer. TGA analyses of the products (Table 4) indicated varying levels of HT (1.6 to 8%), based on the %residue, which is indicative of the amount of alumina and magnesia left after all the carbon sources in the samples volatilized. Indeed the experiments with highest HT gave highest %residue. The first DSC transition temperatures (114-122C) were only small and diffuse peaks and may not be the real polymer transition temperature. It seems likely that the second transition, at 370C, is more likely due to the phase changes in the copolymer, thus indicating the need for higher processing temperatures in polymer applications. These polymers however dissolve or form a clear gel in toluene, ethyl acetate and to a limited extent in methylene chloride. The copolymer with the least amount of HT (1.6% residue by TGA) was the most soluble in toluene. When the solutions dried it left a clear film with good adhesive characteristics.

CONCLUSIONS

New hydrotalcites have been made due to improvements of the original process. Catapal alumina is preferred over FCA as the aluminum source for the synthesis; it seems more

reactive and it leads to HTs with the desired cabbage morphology. With further development of the organic solvent process all the HTs that produced the semi-cabbage can be upgraded to HTs with cabbage morphology.

Whatever their morphology, the true usefulness in polymer applications of these materials can only be determined through polymer blend testings for related physical characteristics.

In production of blends the preferred method is the addition of the polymer emulsion to the HT gel, blended in the water medium then spray dried. This is economical and leads to a more uniform blend than the regelling approach.

Copolymerization of monomers and HTs with anions containing double bonds should be conducted in a medium that will yield a dissolved or finely suspended product.

RECOMMENDATIONS AND FUTURE WORK

For applications that require uniform particles and composition of the final HT the following recommendation is offered:

1) That the first step in the preparation be carried out in an inert organic solvent such as hexane or higher boiling hydrocarbon. The solvent can then be removed followed by the reaction with magnesium oxide in water.
2) That the Catapal alumina be the aluminum source and not FCA.

Uniform blends of HT and polymer should be prepared from the addition of polymer emulsion to the final gel in the HT preparation and not from regelled HT.

Future copolymerization of functional HT and MMA should be carried out in an organic solvent and not in water. Perhaps some of these copolymers should be test for adhesive properties.

The hydrotalcites from methacrylic, acrylic, benzoic, vinylacetic, octanoic and stearic acids are new substances and should be filed for composition of matter. Also the use

of organic solvents in the preparation for water insoluble acids can be considered an improvement of the original patent and should therefore be protected. — claim this

Currently no more HT preparations are planned and any future work would come from future the needs of the polymers group as those needs would be dictated by tests on the HTs and HT-polypropylene blends at hand.

ACKNOWLEDGEMENTS

Acknowledge the help of Jeffrey Uhaul (summer co-op) who was instrumental in carrying a lot of the preparations. Also to Glen Koshinsky who did the spray drying of the HT-polypropylene blends.

Table 1

HYDROTALCITES and PROPERTIES

ANION (A-) SOURCE	d spacing (A)	Interlayer Distance	STEM	SIZE, micron	Sample #
Acetic acid	12.0	7.3	cabbage	6x4	360-16B
Acrylic acid	16.6	11.9	cabbage	3x3	360-19
Stearic acid	19.4	14.6	semi-cabbage	11x6	360-22A
Benzoic acid	17.0	12.2	cabbage	4x3	360-27A
Ethane sulfonic acid	14.8	10.1	cabbage	6x3	360-27B
Glycolic acid	9.2	4.4	clump	2x1	360-21A
Lactic acid	15.0	10.2	semi-cabbage	3x4	360-21B
Gamma-Butyrolactone	12.3	12.3	clump	2x2	360-20
Hexanoic acid	19.2	14.4	clump	5x3	348-18B
Octanoic acid	22.9	18.1	semi-cabbage	5x4	348-19A
Decanoic acid	23.9	19.1	semi-cabbage	4x3	348-19B
methacrylic acid	13.2	8.4	cabbage	6x5	348-31
vinylacetic acid	17.7	12.9	cabbage	6x4	348-32B
Cinnamic acid	18.4	13.6	clumps	7x4	348-42
Octanoic acid	20.3	15.5	cabbage	5x2	348-50
Chlorobenzoic acid	16.8	12.0	cabbage	3x4	348-44
Naphthoic acid	19.2	14.4	semi-cabbage	6x6	348-43

Mixed acids[1]	16.4	11.6	semi-cabbage 6x3	360-54
Mixed acids[2]	15.5	10.7	semi-cabbage 3x2	360-73
Stearic acid[3]	24.4	19.6	semi-cabbage 5x3	360-53
Stearic acid[4]	26.4	21.6	semi-cabbage 3x3	360-65
LaRoche HTC-0498-10	9.7	5.0	semi-cabbage 11x5	360-87

1 mixture molar composition: 1.34 acetic acid, 0.6 hexanoic acid, 0.8 stearic acid
2 mixture molar composition: 3.76 acrylic acid, 1.14 acetic acid, 0.57 stearic acid
3 first step of prep carried out in stearic acid melt without a solvent
4 first step of prep carried out in hexane solvent.

Table 2

HYDROTALCITE AND POLYPROPYLENE BLENDS[1]

%HDROTALCITE	d spacing (A)	DSC MAX.,C	TGA % Residue	Sample #
5	6.3	147, 380	9.6	360-74
9	6.2	147, 374	10.2	360-75
34	6.2	151, 329	22.4	360-79
38	6.2	151, 328	23.5	360-82
81	11.4	149, 331	46.1	360-72

(1) 3% HT gelled in water at about 50C and polypropylene emulsion added to the mixture.

Table 3

HYDROTALCITES AND POLYPROPYLENE BLENDS

ANION SOURCE	% HT	d spacing	d spacing %change	DSC Max.,C	TGA % Residue	SAMPLE #
Acrylic acid[1]	57	13.7	-17.5	152	37.2	360-68
Methacrylic acid[1]	59	15.5	-17.4	150	27.9	360-69
Vinylacetic acid	41	15.5	-11.4	150	23.9	360-83
Octanoic acid	47	23.6	+16.3	151	16.0	360-86
Mixed acids[2]	55	17.0	+3.7	148	26.1	360-86B
Stearic acid	38	17.1	-35.2	149	10.0	360-88

(1) polypropylene emulsion added to unisolated HT in the final mixture. All others were prepared by addition of Previously isolated HT that is regelled then polypropylene emulsion added.

(2) mixed acids composed of 1.34:0.6:0.8 molar ratio acetic, hexanoic and stearic acids.

Table 4

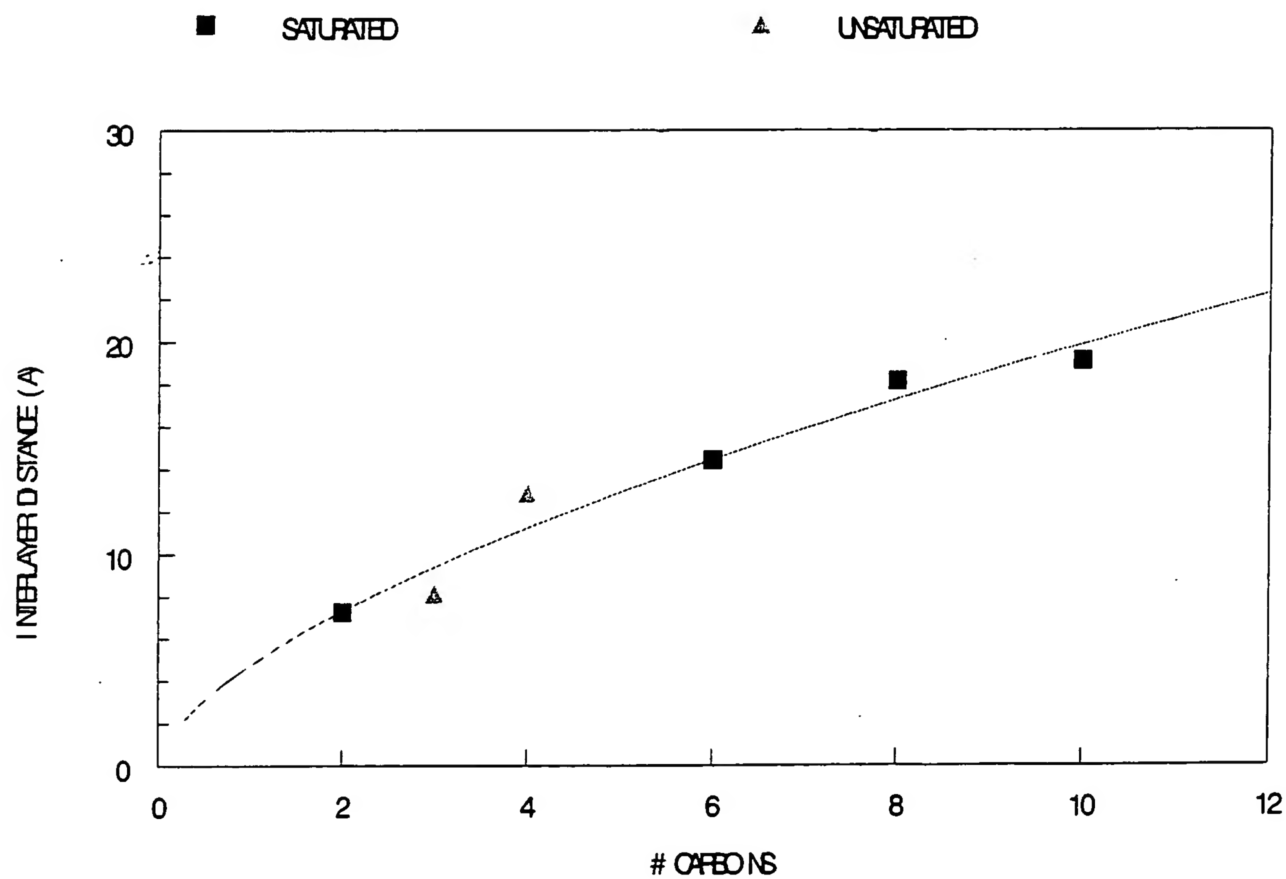
MMA POLYMERIZATION IN PRESENCE OF HT[(1)]

MMA, g	HT,g	RX temp, C	Hrs	Polymer, g	DSC Max, C	TGA % Residue	Sample #
364	30	72-84	4	341	122, 258	3.9	360-60A
306	10	75-90	4	256	115, 372	1.6	360-63
264	30	75-85	4	229	114, 374	7.5	360-63A

(1) Polymer carried out in Chemco reactor under 20 psi N2 400 rpm stirring. Initiator used was AIBN (0.5g) added to the reactor over time in some of the MMA. Surfactant (2.5-3.5g) used was Aerosol OT 75%.

HYDROTALCITE INTERLAYER SPACING (IS)

IS vs CARBONS IN CARBOXYLATE ANION



Reference:

1) Memo from Ed. Restelli to S. A. White, Ed. Nemeth; April 8, 1998.
2) Annual Report, Gas Research Institute, Feb 1988-1989.
3) Proc. Schl. Sci. Toai Univ., 32(1997) 95-104.
4) U.S. Pat. 5,399,329, Aristech Chemical Corporation.
5) Japanese Patent Application: JP 96-189168 960718, Mitsui Toatsu Chemicals, Inc. Japan.
6) Eur. Pat. Application: EP 91-400231 910131, Atochem, Fr.; CAN 116:175424.
7) Japanese Patent Application: JP86-296799 861215, Du Pont-Mitsui Polychemicals Co., Ltd, Japan; CAN 109:151094.
8) Int. SAMLE Symp. Exhib. (1998), 43, 1053-1066; CAN 1998:575663.

ARISTECH

RESEARCH CHARACTERIZATION REPORT

REPORT FOR: Brima, T.	SAMPLE NO.: 98-0703
REQUEST NO.:	DATE RECEIVED: 9/2/98
CUSTOMER:	DATE COMPLETED: 11/19/98
PURPOSE OF WORK: To perform TGA and DSC analyses of the samples.	

TGA

These samples were run with a ramp to 850 °C at a rate of 20 °C/min. The samples were run in duplicate. The numbers in parentheses are individual run values. Sample sizes are in mg, and temperatures are in °C.

For 360-72, on the first run a loss of 11.72% also occurred at 84.97 °C, most likely corresponding to the loss of water. This transition is not seen in the other runs, and this difference is probably due to using the TGA Autosampler, which does not cool completely to ambient temperature between runs.

Sample 360-72 does not have a good separation of the two transitions below, and the second transition is actually a combination of two transitions which are too close to resolve.

	360-72	360-74
Transition 1		
Temperature	331.08 (333.22, 328.93)	380.53 (377.20, 383.85)
% Mass Loss	14.65 (13.99, 15.30)	19.40 (20.63, 18.16)
Transition 2		
Temperature	473.54 (453.47, 493.60)	510.17 (508.94, 511.40)
% Mass Loss	31.43 (28.30, 34.55)	68.85 (67.51, 70.18)
Residue (%)	46.14 (43.50, 48.78)	9.619 (9.513, 9.725)
Sample Size	(13.76, 7.0970)	(4.7340, 3.4560)

	360-75	360-79	360-82
Residue (%)	10.21 (10.08, 10.33)	22.41 (22.27, 22.55)	23.50 (Standard Deviation: 0.73)
Sample Size	(10.9130, 7.5860)	(6.4140, 9.4520)	(6.8030, 9.2960, 17.1240)

DSC

These samples were run with a ramp to 400 °C at a rate of 10 °C/min.

360-75 does not seem to be a uniform sample. It was run five times, with different results each time. There is a consistent peak around 147 °C, though. There is also a consistent peak/ peak grouping occurring around 330 to 340 °C. In several of the runs, a broad peak was seen centered around 200 °C. It appears that there is some violent decomposition occurring at high temperatures for this sample as well.

The other samples were both run twice. Temperatures are in °C, and the individual run values are in parentheses.

	360-79	360-82
Peak One Temperature	151.15 (150.14, 152.16)	151.76 (152.87, 150.65)
Peak Two Temperature	328.88 (327.87, 329.89)	328.60 (329.03, 328.16)

Jennifer V McKnight

J. K. McKnight

cc: J. A. McCormick

Richardson, Karen C.

From: Fujii, Masaki [FujiiM@SunocoChemicals.com]
Sent: Friday, November 09, 2001 1:39 PM
To: 'McWilliams, Matthew P.'
Subject: RE: Manufacturing Inorganic Polymer Hybrids

DataDescriptiveNanoExtruder.do... DataTableExtruder.xls

Matt:

1. Here below are attached two files (one for description and the other for a data sheet) for an example covering the method of exfoliation by rapid vaporization.

2. Other comments
(1) Page 3, Line 8 (and also many other places throughout the specification including Claims)
The description "a mixture comprising at least one molten polymer" sounds illogical to me. If the number of molten polymer is one, it is not considered a mixture (of polymers), although it is a mixture of molecules. Will you please find a better way?

(2). Page 4, Line 19
Instead of "Santoprene® (dynamically cross-linked thermoplastic olefin polymers)", I think we better use generic name "dynamically cross-linked thermoplastic olefin polymers" only.

(3) Page 4, Lines 20 - 22
Please re-write
"Polymers suitable for this invention can also include acid functionalized polymers. Acids commonly used as compatibilizers with non-polar polymers are maleic acid, [insert other preferred acids, if necessary]"
into
"Polymers suitable for this invention can also include acid or ester functionalized polymers. Commonly used modifiers as compatibilizers with non-polar polymers are maleic acid and glycidyl methacrylate. (Please brush up the English.)

(4) Page 5, Lines 19 - 20
Solvents: Water, alcohols such as methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol, acetone, methyl ethyl ketone. The most preferable solvent is water.

(5) Page 6, Line 3
Please re-write
"The formation of the amide or imide group facilitates the interaction between the exfoliated intercalated hydrotalcite and the molten polymer, and maintains dispersion of the exfoliated intercalated hydrotalcite throughout the molten polymer."
into
"The formation of the amide or imide group leads to direct chemical linkage between the exfoliated hydrotalcite platelets and the molten polymer, and reinforce the interface between the exfoliated hydrotalcite platelets and the polymer matrix and improve physical properties of the eventually molded articles." (Please brush up the English.)

(6) Page 6, Lines 5 - 8
The content ranges of hydrotalcite given here are good for the final composites. We need to consider the case in which a master-batch is

prepared first (by a resin manufacturer), and then it is diluted with a polymer (by a compounder or by a molder.) Such a master-batch can contain the hydrotalcite in the rage of 20 % through 80 %. The range can more preferably be 30 % through 60 %. This part may best be handled in or following the paragraph which straddles Pages 6 and 7.

(7) Page 6, Line 15
I will write to you in a separate mail on the examples of inorganic materials.

(8) Page 7, Lines 4 - 5
Please eliminate the sentence: This embodiment of the present invention is advantageous over methods of synthesizing nanocomposites because it can be carried out as a "batch" and not continuous method. It seems there is some misunderstanding of the term "master-batch".

(9) Page 7, Lines 7 - 10
After the sentence "The method eliminates the need for a compatibilizer as a third component in the manufacture of nanocomposites, as the inorganic material is either self-exfoliated or exfoliated by rapid vaporization", please add a concept that such compatibilizers can still contribute to farther degree of exfoliation as shown by the examples.

(10) Claim 1, Line 2
In regards to the phrase "Providing an inorganic material having a layered structure; ", let me point out that if we use self-exfoliated hydrotalcite in the solvent it has lost the layered structure either completely or to a substantially high degree. Some other hydrotalcites, clays and micas, either organo-modified or not, are believed to have more or less layered structure even in a swollen state.

(11) Claim 13
In regards to the expression "... self-exfoliation that is induced by adding said inorganic material to a solvent", let me point out that if we use self-exfoliated hydrotalcite is synthesized in the solvent, the self-exfoliation has not been induced by adding the inorganic material, hydrotalcite, to a solvent.

(12) Claim 19, Lines 1 - 2
In regards to the phrase "Providing an intercalated inorganic material having a layered structure; ", let me point out again that if we use self-exfoliated hydrotalcite in the solvent it has lost the layered structure either completely or to a substantially high degree.

Best regards,
Masaki

-----Original Message-----
From: McWilliams, Matthew P. [mailto:MCWILLIM@pepperlaw.com]
Sent: Wednesday, November 07, 2001 10:04 AM
To: 'fujiim@sunocochemicals.com'
Subject: re: Manufacturing Inorganic Polymer Hybrids

Masaki,

Attached is the first draft of the above captioned application. This application covers the two alternate methods of exfoliating inorganic materials for introduction into nanocomposites; self-exfoliation by addition to a solvent and exfoliation by rapid solvent vaporization.

Please review the attached and provide your comments when convenient. Also, may we expect additional data for an example covering the method of exfoliation by rapid vaporization?

Thanks.

Matt

<<Manufacturing Inorganic Polymer Hybrids .doc>>

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PATENT & TRADEMARK OFFICE

Attorney;s Docket No. 47003.000058

CERTIFICATE OF MAILING UNDER 37 CFR 1.10

Express Mail Label No. EV 306260815 US

Date of Deposit: March 3, 2004

Serial Number: 10/043,934

Filed: January 11, 2002

Applicant: Brima et al.

Title of Invention: Manufacturing Inorganic Polymer Hybrids

I hereby certify that this paper is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to Mail Stop Fee Amendment, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

Katherine V. Hilbert	Katherine V. Hilbert
(Typed or printed name of person mailing paper)	(Signature of person mailing paper or fee)